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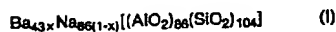
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54 Crystalline zeolite and agglomerate containing the same.

57 A crystalline zeolite having, except for water crystallization, the formula:



wherein X is a number from 0.6 to 0.8. This crystalline zeolite can be mixed with a binder, followed by the calcination. Thus, a zeolitic molecular sieve agglomerate suitable for use in the separation and/or removal of a specific component (e.g., carbon monoxide, oxygen, carbon dioxide, or water vapor) from a fluid stream containing the same.

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CRYSTALLINE ZEOLITE AND AGGLOMERATE CONTAINING THE SAME

BACKGROUND OF THE INVENTION

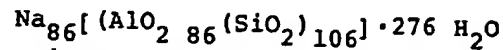
1. Field of the Invention

The present invention relates to a crystalline zeolite, more specifically a barium-exchanged crystalline zeolite X (or a barium cation form type-X crystalline zeolite). The present invention also relates to an agglomerate comprising the above-mentioned crystalline zeolite and a binder material, which is suitable for use as an adsorbent for selective removal and/or separation of a specific component such as carbon monoxide, oxygen, carbon dioxide, and water vapor from a fluid stream containing the same.

2. Description of Related Art

It is well known in the art that natural or synthetic zeolites are industrially utilized for drying, purification, recovery, and/or separation of various fluids such as hydrocarbon streams and atmospheric air employing the adsorptive properties of the components in the fluids on the zeolites. The effectiveness of the treatments of a fluid stream such as drying, purification, recovery and/or separation depends upon the type of zeolite to be used as well as the components of a fluid to be treated. For example, Na-A zeolite (or sodium cation form type-A crystalline zeolite) pellets comprising crystalline zeolite Na-A and a clay mineral as main constituents can adsorb molecules having size and shape to permit entrance through a micro-pore of 3.8 angstroms such as water vapor, hydrogen sulphide, carbon dioxide, ethane, ethyl alcohol and butadiene, while other molecules such as propane, cyclic hydrocarbons and compressor oil being excluded. The Na-A zeolite pellets, therefore, have been advantageously utilized as an adsorbent for such as natural gas and solvent drying, carbon dioxide removal from natural gas streams. Furthermore, Na-X zeolite pellets comprising crystals of Na-X

zeolite having rational formula of:



and a clay mineral as main constituents can adsorb molecules smaller than an effective diameter of 10 angstroms such as iso-paraffins, iso-olefins and di-n-butylamine and exclude molecules having a large diameter of more than 10 angstroms such as tri-n-butylamine, and have been employed for the purposes of for example, simultaneous removal of moisture and carbon dioxide from fluid streams containing the same or the removal of sulphur compounds from hydrocarbon streams containing the same.

It is also known in the art that the entire or partial exchange of the cation in a crystalline zeolite to another has a marked effect on its adsorptivity and cation-exchanged forms of Na-form zeolites such as calcium- and potassium-forms are used depending upon services therewith. Barium-exchanged form zeolites, however, have not been of wide prevalence in industrial services, although some of the said forms have been proposed. For example, barium form zeolite X prepared by exchanging 90% or more of sodium cations in the above-mentioned zeolite Na-X with barium cations is described in, for example, U.S. Patent No. 2,882,244. The Ba-form zeolite X exhibits the desirable separation property for various sorbates such as nitrogen and oxygen. However, the desirable separation property of the conventional barium-form zeolite X is susceptible to be impaired during processing, i.e., the blending of the barium-form zeolite and the binder, the fashioning of the mixture into suitable forms and the firing of the formed material at elevated temperatures has prevented the prevalence thereof in the practical use.

One the other hand, although the above-mentioned Na-X zeolite has been employed for the above-mentioned purpose, for example, as an industrial adsorbent for separation and/or removal, it is still not satisfactory for some uses as an adsorbent, for example, the

separation of carbon monoxide and nitrogen and the separation of oxygen and nitrogen of atmospheric air.

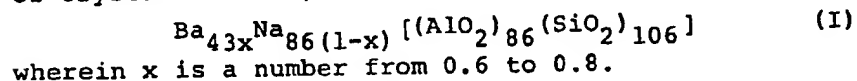
SUMMARY OF THE INVENTION

Accordingly, the object of the present invention is to eliminate the above-mentioned disadvantages of the conventional Na-X zeolite and to provide a barium-exchanged crystalline zeolite X.

Another object of the present invention is to provide a zeolitic molecular sieve agglomerate for the use of effective separation and/or removal of specific components from fluid streams containing the same.

Other objects and advantages of the present invention will be apparent from the following descriptions.

In accordance with the present invention, there is provided a crystalline zeolite having, except for water of crystallization, the formula:



In accordance with the present invention, there is also provided a zeolitic molecular sieve agglomerate comprising a bonded product of a crystalline zeolite having the above-mentioned formula (I) and a binder activated at elevated temperature for the use of separation and/or removal of a specific component from a fluid stream containing the same.

BRIEF DESCRIPTION OF THE DRAWINGS

The present invention will be better understood from the following descriptions presented in connection with the accompanying drawings, in which:

Fig. 1 is an X-ray diffraction pattern of the barium-exchanged crystalline zeolite X obtained in Example 1;

Fig. 2 is an X-ray diffraction pattern of the barium-exchanged crystalline zeolite X obtained in Example 2;

Fig. 3 is an X-ray diffraction pattern of the barium-exchanged crystalline zeolite X obtained in

Example 3;

Fig. 4 is an X-ray diffraction pattern of the barium-exchanged crystalline zeolite X obtained in Example 4;

5 Fig. 5 is an X-ray diffraction pattern of the Na-X zeolite powder used as the starting material in Examples 1 to 4;

Fig. 6 is a chromatogram obtained in Example 10;

10 Fig. 7 is a chromatogram obtained in Comparative Example 4;

Fig. 8 is a chromatogram obtained in Example 11; and

15 Fig. 9 is a chromatogram obtained in Comparative Example 5.

DESCRIPTION OF THE PREFERRED EMBODIMENTS

As mentioned above, the crystalline zeolites according to the present invention are those having, except for the water of crystallization, the general
20 formula (I) and obtained by substituting barium cation for 60% to 80% of the sodium cation of the Na-X zeolite. When the barium cation exchange ratio is less than 60%, the separation property of the sorbates in a fluid stream containing the same is not improved, when the
25 agglomerates prepared by blending the zeolite and a clay binder and activated at elevated temperatures are compared with the conventional Na-X zeolite agglomerates prepared by the same procedure as the above-mentioned Ba-X zeolite agglomerates. Contrary to this, the Ba-X
30 having higher than 80% of cation exchange ratio causes a difficulty in crystalline stability thereof, when manufactured into agglomerates for the industrial use with maintaining the desired adsorptive and/or separation property.

35 The Na-X zeolite used as a starting material in the preparation of the barium-exchanged crystalline zeolite X according to the present invention is known and com-

mercially available, which can also be prepared by the methods disclosed in, for example, U.S. Patent No. 2,882,244 and 2,979,381.

5 The partial barium ion exchange of the Na-X zeolite
can be carried out by, for example, a method disclosed
in U.S. Patent No. 2,882,244. For example, the Na-X
zeolite is treated with a solution containing a certain
amount of barium cation, such as an aqueous or alcoholic
10 solution containing a certain amount of a barium compound
to obtain the desired barium-exchanged crystalline
zeolite X. A 0.1 to 1 mole/liter solution of barium
chloride or barium nitrate can be typically employed in
the preparation of the desired barium-exchanged crystal-
line zeolite X. The desired barium ion exchange ratio
15 of 60% to 80% can be easily achieved by controlling the
relative amounts of the barium compound and the Na-X
zeolite used in the treatment process.

20 The barium-exchanged crystalline zeolite having the
above-mentioned general formula (I) thus prepared can be
advantageously converted into a zeolitic molecular sieve
agglomerate in any conventional manner, for example, by
blending the binders, fashioning the mixture into
suitable forms and activating at elevated temperatures.
Thus, the clay is dried to give a bonded product and the
25 water of hydration of the zeolite is lost. The binders
usable in the present invention include any conventional
binders, for example, bentonite clays such as bentonite,
kaolin clays such as kaolin, plastic ball clays, and
clays of attapulgite.

30 Although there is no specific limitations in the
mixing ratio of the crystalline zeolite and the binder,
the preferable weight ratio of the crystalline zeolite
to the binder is 70:30 to 90:10. The barium-exchanged
crystalline zeolite X and the binder and, optionally,
35 some conventional additives, can be mixed together by
using any conventional mechanical means such as a muller,
kneader, or blender. The mixture is then formed in any

conventional manner, for example, by using an extruder, pelletizer, or any other bead-forming means to pellets or other suitable forms. The resultant agglomerates are finally dried and calcined at elevated temperatures (e.g., 150°C to 300°C and 550°C to 700°C, respectively). Thus, the desired zeolitic molecular sieve agglomerate can be obtained. The water of crystallization (i.e., 276 molecule of water per unit cell) contained in the crystal of the starting Na-X zeolite or the barium-exchanged product thereof is substantially removed to zero during the drying and calcining steps. Thus, the desired molecular sieve agglomerate suitable for use in the drying, adsorption, separation, or removal of a certain gas or other components can be produced.

The molecular sieve agglomerate including the barium-exchanged type crystalline zeolite, in which 60% to 80% of the sodium ions is exchanged with barium ions, can be manufactured by preparing a zeolitic molecular sieve agglomerate including Na-X zeolite and the above-mentioned binder, followed by partially exchanging the sodium ions of the resultant Na-X zeolite agglomerate with barium ions. The Na-X zeolitic molecular sieve agglomerate can be prepared in any conventional manner, e.g., by mixing the Na-X zeolite with the binder, followed by drying and calcining the formed mixture at elevated temperatures (e.g., 150°C to 300°C and 550°C to 700°C, respectively). The resultant Na-X zeolitic molecular sieve agglomerate can be treated with the above-mentioned solution containing barium ions. The resultant barium-exchanged molecular sieve agglomerate is then dried and activated at a temperature of, for example, 200°C to 550°C.

The molecular sieve agglomerates including, as a main constituent, the barium-exchanged crystalline zeolite having the above-mentioned general formula (I) have excellent thermal stability and thermal deterioration resistance and can be effectively used in the separation

and purification of gas mixtures. Especially, the present molecular sieve agglomerates can be advantageously used in the separation of carbon monoxide and nitrogen, in the separation of nitrogen and oxygen, or
5 in the removal of water vapor and carbon dioxide from air containing the same.

The present invention now will be further illustrated by, but is by no means limited to, the following Examples.

10 Example 1

A 100 g amount (dry weight) of Na-X zeolite powder available from UNION SHOWA K.K. was saturated with moisture in ambient conditions. Then, the Na-X zeolite powder was slurried by adding 250 ml of water. An aqueous
15 solution of 50 g of $\text{BaCl}_2 \cdot 2\text{H}_2\text{O}$ having a purity of 98.5% in 250 ml of water was added to the above prepared slurry. The mixture was then allowed to stand, while occasionally stirring, at room temperature for one night.

The crystal thus obtained was filtered and thoroughly washed with water until no chlorine ions were detected
20 in the washed liquor. After air dried, the crystalline zeolite was heated at a temperature of 200°C for 2 hours and, then at a temperature of 450°C for 2 hours. Thus, the crystalline zeolite was activated.

25 The zeolite crystal thus prepared had a barium content of 21.85% by weight determined by gravimetric analysis and a sodium content of 4.47% by weight determined by atomic-absorption spectroscopic analysis. The barium ion exchange ratio calculated from these analysis
30 data was 62%.

The X-ray diffraction pattern of the barium-exchanged crystalline zeolite obtained above was as shown in Fig. 1. The lattice spacings calculated from each peak of Fig. 1 were fundamentally consistent with
35 those of Ba-X disclosed in U.S. Patent No. 2,882,244, except that there were strong peaks at $a = 7.57 \text{ \AA}$ and 3.83 \AA , which are strongly observed in the case of Na-X.

For comparison, the X-ray diffraction pattern of the starting molecular sieve 13X powder in Fig. 5. The reason why the peak height of the X-ray diffraction pattern in Fig. 1 is lower than that of the molecular sieve 13X powder is that the X-ray absorption coefficient of barium is large.

It is clear from the above data that the sodium ions of the starting Na-X zeolite were partially exchanged with barium ions.

The water absorption capacity of the barium-exchanged crystalline zeolite obtained above was 27.3 g/100 g, as determined under the conditions of 17.5 mmHg and 25°C in a McBain Bakr apparatus. Although this water adsorption capacity was lower than that of the starting Na-X zeolite powder (i.e., 33.3 g/100 g), this was caused by the fact that the specific gravity of the crystalline zeolite was increased and that the internal void volume of the crystals per unit cell was changed due to the exchange of sodium ion with the barium ion. When the adsorption capacity was compared in terms of the adsorption amount per unit cell, there was no substantial difference between the water adsorption capacities.

Example 2

Barium-exchanged crystalline zeolite was prepared in the same manner as in Example 1, except that 60 g of $\text{BaCl}_2 \cdot 2\text{H}_2\text{O}$ was used.

The barium content and the sodium content of the resultant crystalline zeolite determined in the same manner as in Example 1 were 22.79% by weight and 4.04% by weight, respectively. The barium ion exchange ratio obtained from these data was 65%. The X-ray diffraction pattern of the crystalline zeolite obtained above was as shown in Fig. 2.

The water absorption capacity of the crystalline zeolite was 26.9 g/100 g as determined in the same manner as in Example 1.

Example 3

Barium-exchanged crystalline zeolite was prepared in the same manner as in Example 1, except that 80 g of $\text{BaCl}_2 \cdot 2\text{H}_2\text{O}$ was used.

5 The barium content and the sodium content of the resultant crystalline determined in the same manner as in Example 1 were 25.92% by weight and 2.89% by weight, respectively. The barium ion exchange ratio obtained from these data was 75%. The X-ray diffraction pattern
10 of the crystalline zeolite obtained above was as shown in Fig. 3.

The water adsorption capacity of the crystalline zeolite was 26.6 g/100 g as determined in the same manner as in Example 1.

15 Example 4

Barium-exchange crystalline zeolite was prepared in the same manner as in Example 3, except that the mixture was heated at a temperature of 80°C for 1 hour after adding the barium solution, instead of being allowed to
20 stand for one night.

The barium content and the sodium content of the resultant crystalline zeolite determined in the same manner as in Example 1 were 25.62% by weight and 2.95% by weight, respectively. The barium ion exchange ratio
25 obtained from these data was 74%. The X-ray diffraction pattern of the crystalline zeolite obtained above was as shown in Fig. 4.

The water adsorption capacity of the crystalline zeolite was 26.5 g/100 g as determined in the same
30 manner as Example 1.

Example 5

A 8 kg amount of barium-exchanged crystalline zeolite X having a barium ion exchange ratio of 66% prepared in the same manner as in Example 2 was saturated
35 with moisture in ambient conditions. The crystalline zeolite thus obtained was mixed with 2 kg of attapulgite by adding 2.7 kg of water. The resultant mixture was

extruded through a die and broken into pellets having a diameter of 1.6 mm.

The pellets obtained above were heated at a temperature of 200°C for 2 hours and were, then, calcined at a temperature of 650°C for 2 hours for the activation. The pellets thus obtained were crushed to the particles having a size of 60 to 80 meshes in terms of Tyler mesh. The CO/N₂ separation capacity of the resultant agglomerate particles was determined by gas chromatography. That is, the separation coefficient defined by a ratio of the retention times of CO/N₂ was 3.90, when 1 ml of a gas mixture (CO/N₂=1/2 by volume) was passed through a gas chromatograph column packed with the above-prepared agglomerate particles under the conditions of a column temperature of 40°C and a feed rate of 30 ml/min with a helium carrier gas and a thermal conductivity detector (TCD). The column diameter was 3 mm and the packed height was 0.5 m.

Furthermore, the water adsorption capacity and the CO₂ adsorption capacity of the agglomerate particles determined in the same manner as in Example 1 were 23.6 g/100 g and 17.0 g/100 g, respectively.

Example 6

A 8 kg amount of barium-exchanged crystalline zeolite having a barium ion exchange ratio of 77% prepared in the same manner as in Example 3 was agglomerated in the same manner as in Example 5. Thus, the agglomerate particles having a size of 60 to 80 meshes were obtained.

The CO/N₂ separation coefficient of the resultant agglomerate particles, determined in the same manner as in Example 5, was 3.75. The water adsorption capacity and the CO₂ adsorption capacity of the agglomerate particles, determined in the same manner as in Example 1, were 22.5 g/100 g and 15.9 g/100 g, respectively.

Comparative Example 1

Barium-exchanged crystalline zeolite was prepared

in the same manner as in Example 1, except that 25 g of $\text{BaCl}_2 \cdot 2\text{H}_2\text{O}$ was used.

5 The barium content and the sodium content of the resultant crystalline zeolite determined in the same manner as in Example 1 were 14.7% by weight and 6.2% by weight, respectively. The barium ion exchange ratio obtained from these data was 44%.

The agglomerates of the barium-exchanged Na-X zeolite were prepared in the same manner as in Example 5.

10 The CO/N_2 separation coefficient of the resultant agglomerate particles, determined in the same manner as in Example 5 was 3.53. The water adsorption capacity and the CO_2 adsorption capacity of the agglomerate particles, determined in the same manner as in Example 1,
15 were 24.7 g/100 g and 16.9 g/100 g, respectively.

Comparative Example 2

Barium-exchanged crystalline zeolite was prepared in the same manner as in Example 1, except that 200 g of $\text{BaCl}_2 \cdot 2\text{H}_2\text{O}$ was used.

20 The barium content and the sodium content of the resultant crystalline zeolite determined in the same manner as in Example 1 were 27.9% by weight and 0.7% by weight, respectively. The barium ion exchange ratio obtained from these data was 93%.

25 The water absorption capacity of the crystalline zeolite was 21.5 g/100 g as determined in the same manner as in Example 1.

Example 7

A 2 kg amount of Na-X zeolite in the form of
30 pellets having a diameter of 1.6 mm (available from UNION SHOWA K.K.) was saturated with moisture in ambient conditions. Then, the hydrated pellets were dipped in a solution of 1 kg of $\text{BaCl}_2 \cdot 2\text{H}_2\text{O}$ dissolved in 10 liters of water and were allowed to stand, with occasionally
35 stirring, at room temperature for one night.

The pellets thus obtained was filtered and thoroughly washed with water until no chlorine ions were detected

in the washed liquor. After air dried, the pellets were heated at a temperature of 200°C for 2 hours and, then at a temperature of 450°C for 2 hours. Thus, the pellets were activated.

5 The barium content and the sodium content of the resultant pellets determined in the same manner as in Example 1 were 18.8% by weight and 3.6% by weight, respectively. The barium ion exchange ratio obtained from these data was 64%.

10 The CO/N₂ separation coefficient of the resultant pellets, determined in the same manner as in Example 5, was 3.86. The water adsorption capacity and the CO₂ adsorption capacity of the pellets, determined in the same manner as in Example 1, were 22.7 g/100 g and
15 15.9 g/100 g, respectively.

Example 8

A 1.8 kg amount of the barium-exchanged crystalline zeolite agglomerate particles prepared in Example 6 above was packed into a adsorption column having a
20 nominal diameter of 50 mm and a length of 1100 mm. A gas mixture of air, water vapor, and carbon dioxide (CO₂ = 340 to 440 ppm by volume, H₂O = saturated at 25°C, and 5 kg/cm²G) was passed through the column at a flow rate of 3.8 Nm³/hr.

25 As a result, the CO₂ adsorption capacity at the CO₂ stoichiometric point was 2.84 g/100 g of zeolite and the mass transfer zone was 23.0% of the total amount of the packed zeolite particles. No breakthrough of the water vapor was observed during the test operation.

30 Example 9

The adsorption test was carried out in the same manner as in Example 8, except that the agglomerate pellets obtained in Example 7 were used.

35 The CO₂ adsorption capacity at the CO₂ stoichiometric point was 2.8 g/100 g of the zeolite and the mass transfer zone was 23.3% of the total amount of the packed zeolite pellets. No. breakthrough of the water

vapor was observed during the test operation.

Comparative Example 3

The adsorption test was carried out in the same manner as in Example 8, except that Na-X zeolite commercially available from UNION SHOWA K.K. were used.

The CO₂ adsorption capacity at the CO₂ stoichiometric point was 2.5 g/100 g of the zeolite and the mass transfer zone was 28% of the total amount of the packed zeolite pellets. No breakthrough of the water vapor was observed during the test operation.

Example 10

The barium-exchanged molecular sieve 13X pellets having a barium exchange ratio of 78% obtained in the same manner as in Example 7, were packed into a gas chromatography column having a nominal diameter of 3 mm. The packed height was 500 mm.

A gas mixture of carbon monoxide and nitrogen (i.e., CO/N₂ = 1/2 by volume) was passed through the column under a pressure of 0.6 to 0.7 kg/cm²G. The resultant chromatogram was as shown in Fig. 6.

Comparative Example 4

The separation test of carbon monoxide and nitrogen was carried out in the same manner as in Example 10, except that the commercially available Na-X zeolite was packed in the column.

The resultant chromatogram was shown in Fig. 7.

Example 11

The separation test of nitrogen and oxygen from air was carried out in the same manner as in Example 10, except that the zeolite particles X having a barium exchange ratio of 65% and air were used as the adsorbent and the gas mixture, respectively.

The resultant chromatogram was as shown in Fig. 8.

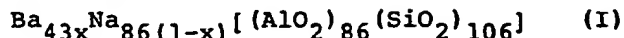
Comparative Example 5

The separation test of Comparative Example 4 was repeated, except that the air was used as a gas mixture.

The resultant chromatogram was as shown in Fig. 9.

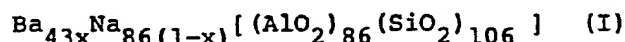
CLAIMS

1. A crystalline zeolite having, except for water of crystallization, the formula:



wherein x is a number from 0.6 to 0.8.

5 2. A zeolitic molecular sieve agglomerate for removing at least one specific component from a fluid stream containing the same comprising a bonded product of a crystalline zeolite and a binder, said crystalline zeolite having, except for water of crystallization, the
10 formula:

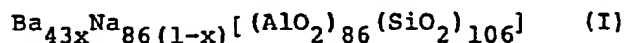


wherein x is a number of 0.6 to 0.8.

3. A zeolitic molecular sieve agglomerate as claimed in claim 2, wherein said binder is bentonite
15 clay, kaolin clay, plastic ball clay, or clay of attapulgite.

4. A zeolitic molecular sieve agglomerate as claimed in claim 2, wherein the weight ratio of the crystalline zeolite to the binder is 70:30 to 90:10.

20 5. A process for removing at least one specific component from a fluid containing the same comprising treating the fluid with a zeolitic molecular sieve agglomerate comprising a bonded product of a crystalline zeolite and a binder, said crystalline zeolite having,
25 except for water of crystalline, the formula:



wherein x is a number from 0.6 to 0.8.

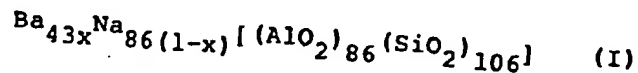
6. A process as claimed in claim 5, wherein carbon monodioxide is separated from a gas mixture
30 containing carbon monoxide and nitrogen.

7. A process as claimed in claim 5, wherein oxygen is separated from a gas mixture containing nitrogen and oxygen.

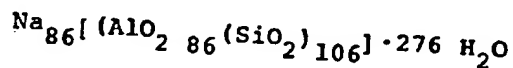
8. A process as claimed in claim 5, wherein
35 carbon dioxide and water vapor are simultaneously removed from a gas mixture containing the same.

CLAIMS FOR THE CONTRACTING STATE AUSTRIA

1. A process for producing a crystalline zeolite having, except for water of crystallization, the formula

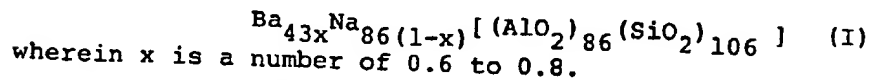


5 wherein x is a number from 0.6 to 0.8,
in which Na-X zeolite having the formula



is subjected to a ion exchange treatment in which 60
to 80 % of the sodium cations are substituted by
10 barium cations.

2. A zeolitic molecular sieve agglomerate for removing at least one specific component from a fluid stream containing the same comprising a bonded product of a crystalline zeolite and a binder, said crystalline
15 zeolite having, except for water of crystallization, the formula:



3. A zeolitic molecular sieve agglomerate as
20 claimed in claim 2, wherein said binder is bentonite clay, kaolin clay, plastic ball clay, or clay of attapulgite.

4. A zeolitic molecular sieve agglomerate as
25 claimed in claim 2, wherein the weight ratio of the crystalline zeolite to the binder is 70:30 to 90:10.

5. A process for removing at least one specific component from a fluid containing the same comprising treating the fluid with a zeolitic molecular sieve agglomerate comprising a bonded product of a crystalline
30 zeolite and a binder, said crystalline zeolite having,

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except for water of crystalline, the formula:

$$\text{Ba}_{43x}\text{Na}_{86(1-x)}[(\text{AlO}_2)_{86}(\text{SiO}_2)_{106}] \quad (\text{I})$$

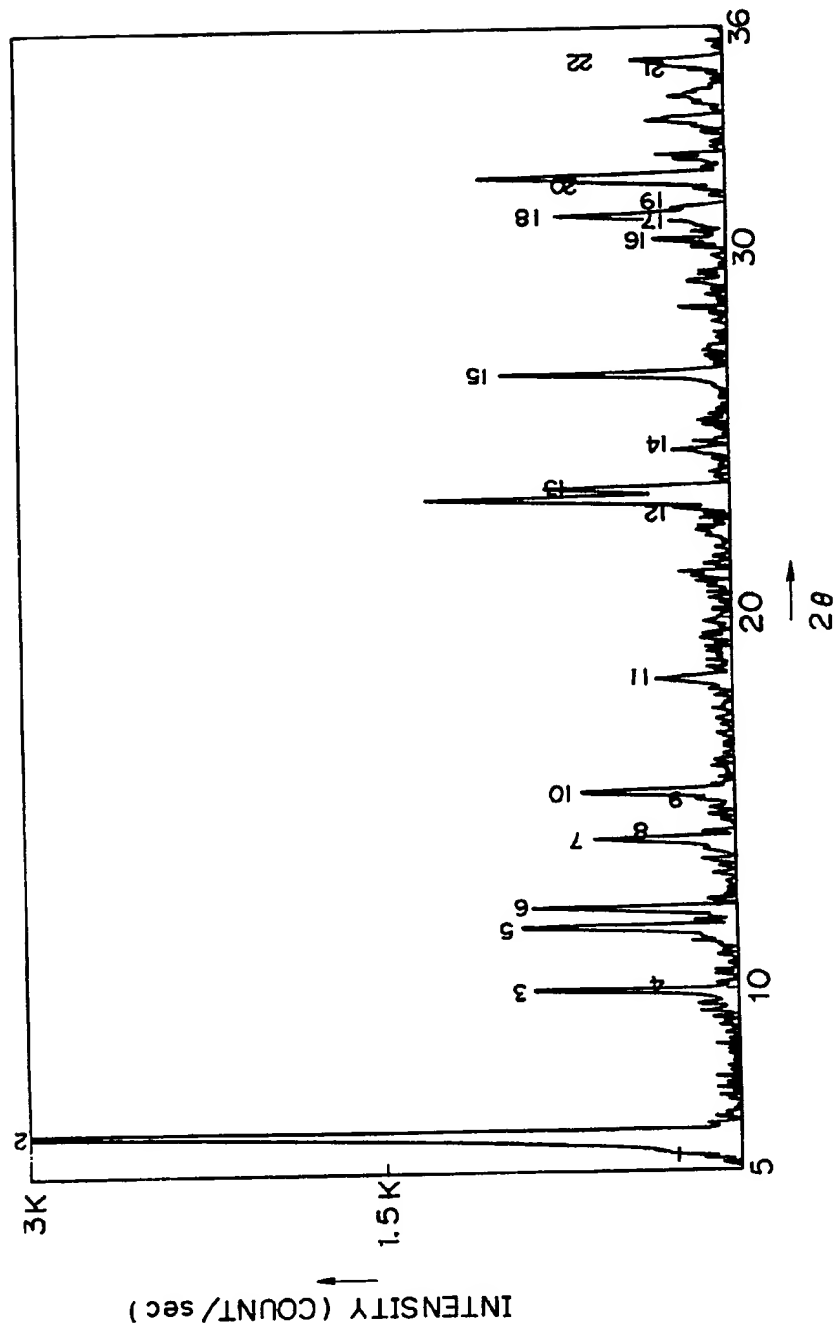
 wherein x is a number from 0.6 to 0.8.

5 6. A process as claimed in claim 5, wherein
 carbon monodioxide is separated from a gas mixture
 containing carbon monoxide and nitrogen.

7. A process as claimed in claim 5, wherein
 oxygen is separated from a gas mixture containing
 nitrogen and oxygen.

10 8. A process as claimed in claim 5, wherein
 carbon dioxide and water vapor are simultaneously
 removed from a gas mixture containing the same.

Fig. 1



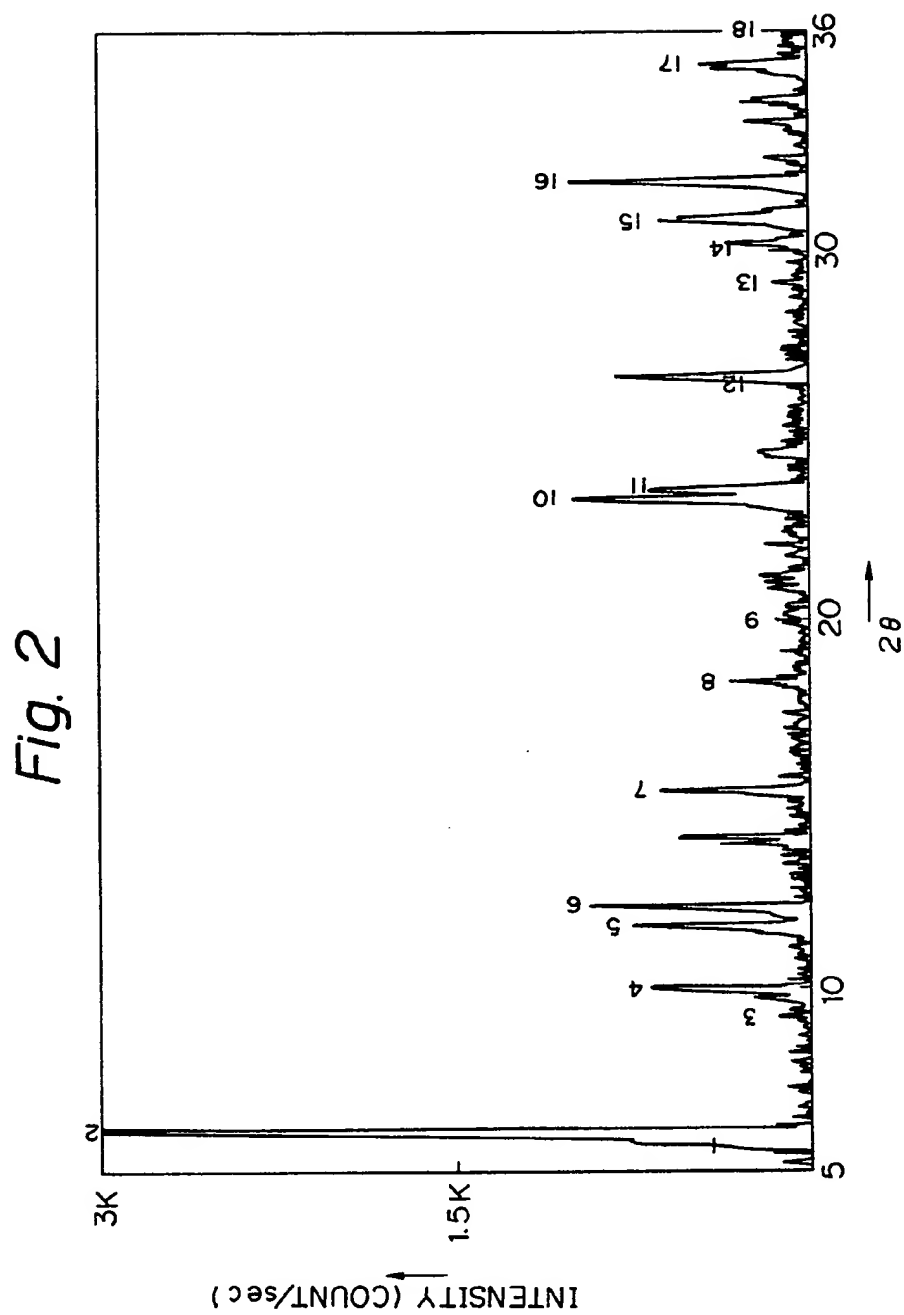


Fig. 3

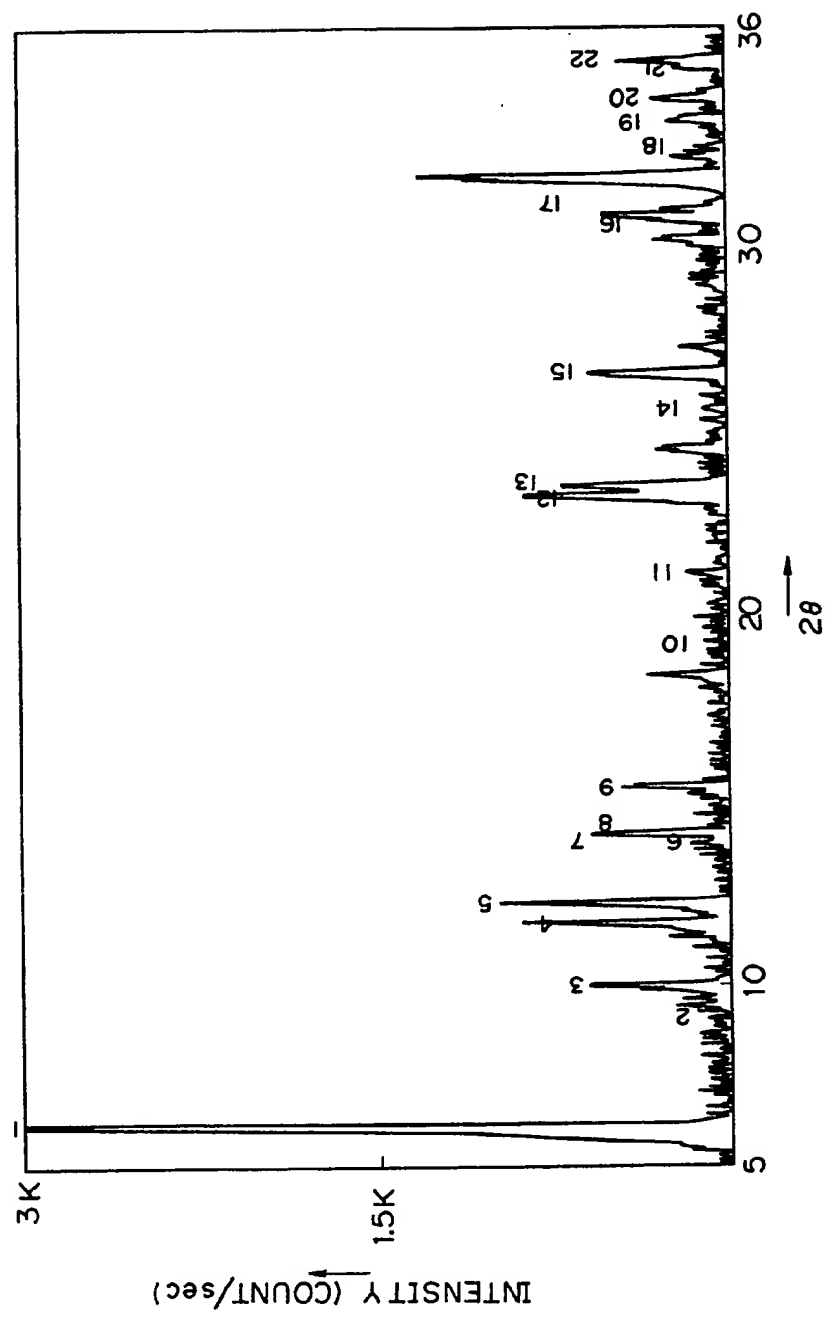


Fig. 4

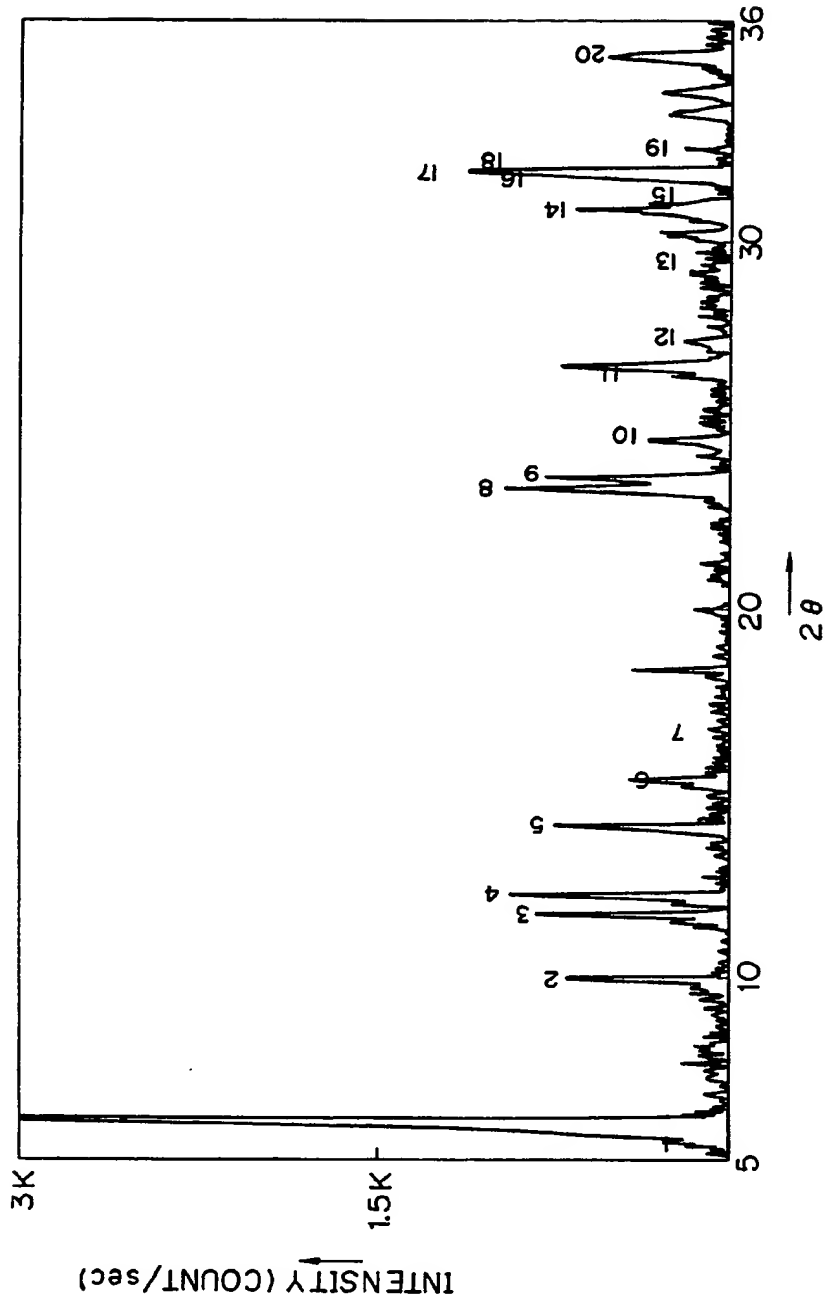


Fig. 5

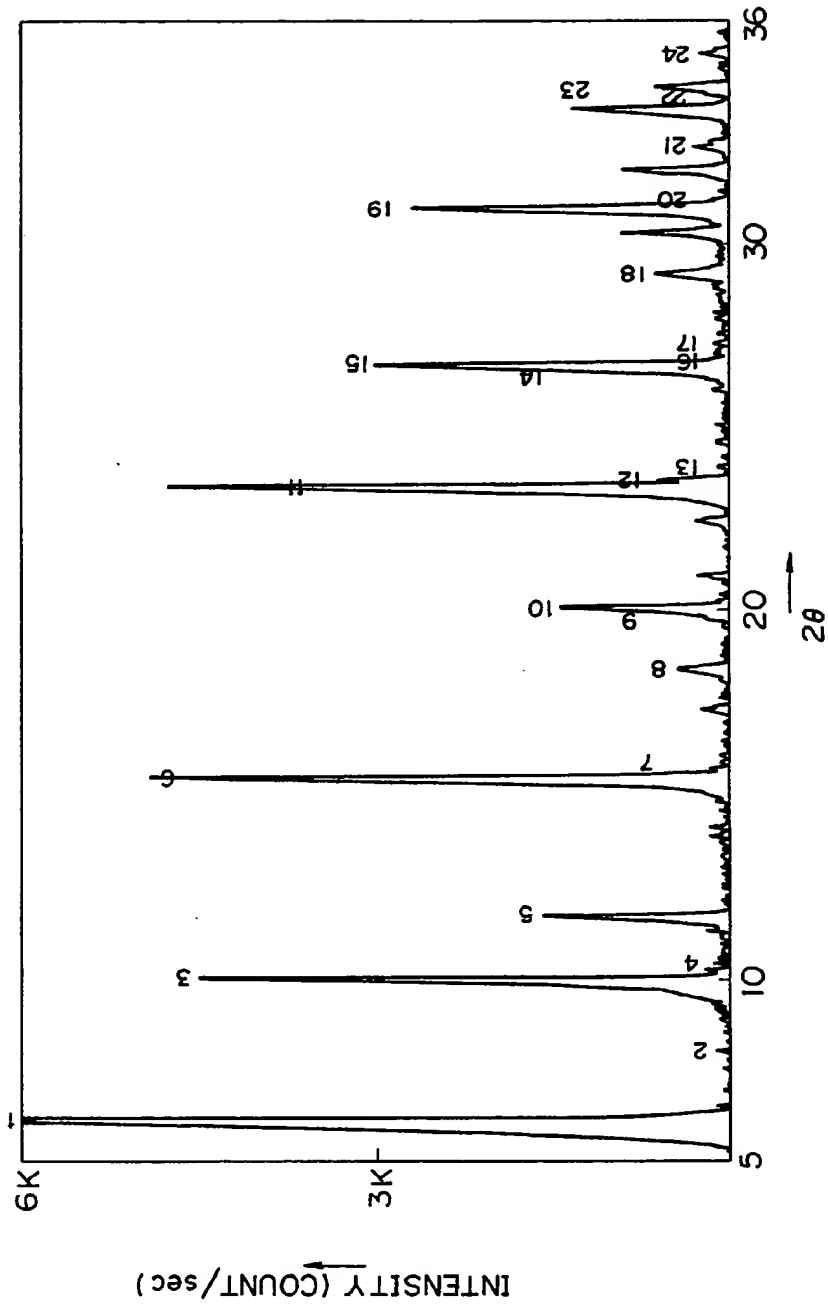


Fig. 6 Fig. 7 Fig. 8 Fig. 9

